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(21) International Application Number: PCT/FI92/00094 (22) International Filing Date: 31 March 1992 (31.03.92) (30) Priority data: 911650 5 April 1991 (05.04.91) FI (71) Applicant (for all designated States except US): KEMIRA OY [FI/FI]; P.O. Box 44, SF-02271 Espoo (FI). (72) Inventors; and (75) Inventors/Applicants (for US only) : VAPAAOKSA, Pekka [FI/FI]; Kirjasniemi 9, SF-37600 Valkeakoski (FI). ROS-SI, Veikko [FI/FI]; Paino 2, SF-37600 Valkeakoski (FI). (74) Agent: BERGGREN OY AB; P.O. Box 16, SF-00101 Helsinki (FI).		(81) Designated States: AT, CA, DE, GB, JP, SE, US. Published <i>With international search report.</i>
(54) Title: A CELLULOSE-BASED FIBRE (57) Abstract The object of the present invention is a product, which contains cellulose and can be a fibre or textile structure with large porosity and swelling capacity.		

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A CELLULOSE-BASED FIBRE

This invention concerns a new, significantly cellulose-based fibre with high absorption and porous structure and/or a textile structure with the said properties and a method for the production of the above-mentioned items. It was surprisingly perceived that a viscose fibre which contains silicic acid, in itself a commercial product, can be modified by alkaline extraction to produce a porous cellulosic fibre with completely new characteristics compared with already known cellulosic fibres.

Demands of high-performance fibres in textile technology have recently increased. Frequently an attempt to meet them has been sought through the production of hybrid fibres. A hybrid fibre is one which is formed from a blend of two or more substances and which has properties which are not owned by the component parts of the hybrid fibre on their own.

One such hybrid fibre is a viscose fibre which contains silicic acid. Such fibres have been studied from the early 1960s, which is when the production technology was broadly-speaking developed. The fibre is spun using a known process, disclosed in more detail in US Patent 3565749.

It has been rapidly learnt how to manufacture a ceramic fibre from this viscose - silicic acid fibre through removal of the cellulose component by pyrolysis. In this process the silicic acid combusts to form silica dioxide and the fibre or fibre structure acquires characteristics resembling those of glass. This technology is also disclosed in US Patent 3565749.

Cellulose has the characteristic of water imbibition and retention. For this reason it is used for a number of technical purposes. Attempts have been made to increase the imbibition and retention characteristics of viscose fibre in particular by

either a chemical or a mechanical treatment. The porosity of the fibre has been affected very little other than by the addition of chemical substances to the fibre material.

The invention currently described concerns a cellulosic fibre made by first manufacturing a hybrid fibre of cellulose and silicic acid and then removing the silica dioxide from the fibre structure. In the first stage the two components of the hybrid fibre are homogeneously distributed in the same phase. The silicic acid content is preferably 10 - 45 percent by weight. From the hybrid fibre the silicic acid is dissolved out preferably with sodium hydroxide, but it is known that silicic acid also dissolves in hydroxides of other alkali metals.

According to this invention the fibre is preferably manufactured by changing the silicic acid to water-glass, which in turn can be returned to the starting point of the process in order to produce viscose which contains silicic acid. A special feature of this procedure is that it allows the production of extremely thin and highly absorbent fibres. As the content of silicic acid in the precursor fibre may be as high as 45 percent, the thickness of the resultant fibre decreases by at least a like proportion. Thus if a conventional cotton-type fibre is manufactured with a thickness of on average 10 μm , the average thickness decreases to a maximum of 6 μm . Without using this part of the production process, the manufacture of cellulosic fibres in such fineness is extremely difficult and expensive.

Examination of other methods for the production of absorbent viscose fibres reveals the best-known commercially available fibre to be Courtaulds' Fibre ML, in which modification of the surface has achieved a fibre with almost as good absorption characteristics as the fibre in this invention. However, the Courtaulds' fibre can be manufactured and is commercially

available only in a form substantially thicker than cotton-type fibre and can therefore not be sold for markets requiring the fine-titre fibre. In the case of Fibre ML the thickness also limits its tenacity or strength, which is substantially below that of a conventional viscose fibre. The tenacity of the individual fibre is so low as to inhibit fine fibre processing on textile systems for which these fibres are intended. The tenacity of the fibre described in this invention, on the other hand, is in principle equal to that of a corresponding conventional viscose fibre, and the minimum limit of processing fineness is substantially lower. This aspect of fineness is of extreme significance in the development of commercial applications.

Highly absorbent cellulosic fibres can no doubt be manufactured by other methods, but their absorption characteristics show differences in quality owing to the size of pores in fibres otherwise manufactured and to other aspects of the fibres' behaviour.

Patent GB 1 390 061 and applications GB 2 224 756 A and GB 2 024 827 A relate to different products from the subject of this invention. The first-mentioned GB 1 390 061 is concerned not with fibre but with the manufacture of viscose sponges, albeit by a new method. Viscose sponges cannot be used as fibres in textile processing: they are cut into blocks for use in various absorption applications such as washing. Application GB 2 224 756 A concerns fibres which have been impregnated with a ceramic material into their existing pores in order to give the fibre new surface characteristics. This filling of the pores neither increases the number of pores in the fibre nor permits of a change in the technical characteristics of the fibre through subsequent removal of the ceramic component, and the patent application therefore bears no resemblance to the product which is the subject of the present invention.

In the method disclosed in patent application GB 2 024 827 A silica (SiO_2) particles are mixed with polyvinyl alcohol and subsequently extracted from the finished product. The extraction of silica particles takes place at a slow rate.

After the removal of the silicic acid it was discovered that the remaining porous cellulosic fibre was stronger and thinner and had greater absorption than the original hybrid fibre. Even more significant is the fact that chemically it is pure cellulose. For this reason the fibre is more suitable than normal viscose for applications such as filters and hygienic waddings.

The silicic acid can be removed from the fibre either at the fibre manufacturing stage or at any subsequent textile processing stage. The removal in fibre treatment after the fibre coagulation and before the fibre enters a textile process has the advantage that silicic acid is not present in the subsequent process. If on the other hand the silicic acid is removed at a later stage of the textile processing, the removal can be naturally associated with other later processing such as the Eisenhut method described below or normal textile mercerising as spun yarn or cloth. Irrespective of the stage at which silicic acid removal takes place, the by-product obtained is water-glass (sodium silicate) which can be refined in the manner usual for that substance.

Removal of the silicic acid is particularly advantageous in the manufacture of nonwovens. Nonwovens production avoids the usual textile processes by using other binding methods such as mechanical carding. There are various binding methods. One such is to establish hydrogen bonds between the fibres by a chemical treatment. One method to achieve this is known as causticising (Eisenhut) where the fibre mat is first treated with caustic soda and the alkaline fibre mat is then neutralised, for example with sulphuric acid. The salts thus formed are then washed out. The product is a very pure viscose nonwoven which

is suitable for clinical and other applications requiring a high level of absorption. Using the method here disclosed provides the advantage that the silicic acid removal and the causticising bonding take place using the same equipment and almost contemporaneously.

According to the present invention the fibres were substantially freed from the silicic acid by using caustic soda preferably in about a 1-normal solution, the quantity of solution being at least equal to the quantity of fibre but most preferably about twice the quantity of fibre.

The following examples describe the invention but are not regarded as limiting the invention.

Example 1

20 g of dry silica dioxide base (99.4% SiO_2) was dissolved in 80 g of 16.8% caustic soda solution. 20 g of the SiO_2 -containing NaOH solution was mixed with 80 g of viscose. The viscose contained 5.5% NaOH and 10.2% alphacellulose, and its viscosity was 6.0 Pas. The result was an SiO_2 -viscose solution containing 3.97% SiO_2 , 8.16% alphacellulose and 7.9% NaOH. The viscosity of the solution was 5.5 Pas. Air and gas bubbles were removed from the solution by pressure, after which the solution was pumped through spinnerette perforations (70 μm) into a spinning bath containing 10% H_2SO_4 , 20% Na_2SO_4 and 0.5% ZnSO_4 .

The fibre tow can be stretched and spun into a viscose fibre which contains silicic acid. The porous fibre according to this invention is obtained by immersing the intermediate fibre in a solution of caustic soda which causes the silica dioxide present to dissolve to water-glass, itself a usable product.

After compression, washing and a solidification stage taking place in a bath containing sulphuric acid, a surprisingly strong fibre is obtained with a highly porous structure.

Example 2

On experimentation with the ability of the new fibre described in the invention to be bonded using the Eisenhut nonwoven bonding system, the new fibre was compared with ordinary nonwoven fibre. The trials were carried out on a laboratory scale applying known conditions used for the bonding of viscose fibre webs.

The trial conditions were as follows:

- fibres 1.7 dtex/40 mm
2.5 dtex/50 mm
- card slivers: fibres carded on Memmingen laboratory card, overlaying 30 cm wide slivers until the sliver weight was about 70 g/m². From this sliver a sample about 30 cm in length was taken for bonding trials
- bonding: the slivers were placed between metal mesh supports and immersed in an NaOH solution where the concentrations, temperatures and immersion times varied as follows:
 - NaOH concentration 5%, 9% and 10% NaOH
 - temperature 22° and 30°C
 - immersion times 20 s and 30 s

The combinations used in the different trials are shown in table 1. After causticisation the slivers were neutralised by immersion in a weak solution of sulphuric acid, concentration 1% H₂SO₄. The slivers were finally rinsed with acid-neutral water.

The results of the tenacity tests carried out on the slivers from the initial trials are presented in table 1.

Table 1

Results of caustic bonding trials carried out on fibres according to the invention and on commercial viscose fibres

TRIAL No.	FIBRE	m ² MASS g	NaOH %	TEMPERA- TURE °C	TIME s	TENA- CITY N	EXTEN- SION %
1	Invention fibre	70	5	22	30	0.4	31
2	"-	97	9	30	20	1.8	15
3	"-	103	10	22	20	1.3	25
4	ordinary commercial viscose	62	5	22	30	0.6	52
5	"-	98	9	30	20	13	13
6	"-	100	10	22	20	-	-

The results show that the product according to the invention is very suitable for further processing.

Example 3

A series of extraction trials was carried out, each using 100 g of viscose fibre which contained silicic acid. Table 2 shows the trials. Fibre produced according to the invention is most favourably generated at about 60°C using 1-normal caustic soda solution.

Example 3a

Table 2

Trials:

100 g 1.7 dtex/40 mm viscose fibre containing silicic acid at 30% SiO₂

Na ₂ O	Concentration	Temperature °C
50 g	0.5 n	40
100 g	1 n	80
30 g	2 n	60
100 g	0.5 n	40

Example 3b As above but fibre 3.5 dtex/80 mm, SiO₂ 33%

Example 3c As above but fibre 8.0 dtex/80 mm, SiO₂ 49%

Results:

	Before extraction			After extraction		
	a	b	c	a	b	c
- dtex	1.7	3.5	8.0	1.1	2.3	2.2
- length	40	80	80	40	80	80
- tenacity cN/dtex	1.7	1.5	1.4	2.5	2.2	2.0
- elongation	20	25	25	18	23	21
- swelling	49	50	48	110	112	110
- ash %	30	33	49	0.4	0.5	0.5

dioxide quantity to 50% gives swelling values between 135 and 140.

The fibre and the textile structures which are the subject of this invention are thus possessed of fast and substantial imbibition, are easily biodegradable, and provide a product of sufficient strength for many applications. The surprising imbibition values probably result from the pores created in the structure by the removal of the silica dioxide, some of these pores being shown to be micropores on the basis of the dyeability trials.

The expression "titre" used in the claims refers to the relationship between the weight and the length of a fibre. It is calculated as follows:

$$1 \text{ dtex} = 10,000 \text{ m/g}$$

$$\text{Tex} = 1 \text{ g} = 1000 \text{ m fibre}$$

If the silica dioxide is removed from the fibre before further processing, the titre declines in a favourable manner. If the silica dioxide is removed only after spinning of yarn, the spun yarn becomes finer.

TESTING FOR POROSITY OF NaOH-EXTRACTED FIBRE

The porosity of the caustic soda extracted fibre (fibre 2), of the original unextracted hybrid fibre (fibre 1) and of a normal viscose fibre (fibre 3) was tested by measurement of their fast swelling. For the same purpose these fibres were dyed with an ordinary viscose test dye to show their dyestuff take-up.

The results are presented in the following table.

TEST	FIBRE 1	FIBRE 2	FIBRE 3
Swelling, %	49	110	90
Dyeability L*	61	45	65
Y	29	14	34

The results show that the caustic-extracted fibre had a higher swelling value than the other fibres, in other words a greater ability to retain water in its structure, which indicates greater porosity in its structure.

A greater difference in porosity was noticeable in the dyeing tests. Of the dyed fibres the caustic-extracted fibre gave the lowest L* value or brightness value. This is to say that it dyed to a deeper shade, indicating the availability of a greater surface area or porosity.

The same is revealed by the other brightness measurement, Y.

On the basis of the above evidence it can be concluded that extraction of the viscose-silicic acid fibre with a solution of caustic soda allows the production of a fibre with a cellulose base and an increased porosity and specific surface area. It has also been observed that the swelling value for the cellulosic fibre is in direct proportion to the content of silica dioxide in the hybrid fibre. With a 28% silica dioxide in the hybrid fibre, a swelling value of 110 is obtained after extraction with caustic soda, while increasing the silica

CLAIMS

1. A product based on porous cellulose and possessed of high swelling and absorption, characterised in that it is achieved by removal by the use of an alkali of silicic acid from the known fibre of viscose which contains silicic acid.
2. A product according to claim 1, characterised in that after fibre spinning the silicic acid is removed by alkali from the fibre only after processing of the fibre into a textile or nonwoven structure.
3. A product according to claim 1 or 2, characterised in that the nonwoven structure is bonded simultaneously with the alkaline extraction of the silicic acid.
4. A product according to claim 1 or 2, characterised in that the titre of the precursor fibre decreases by at least the same percentage as the original silicic acid content of the precursor fibre.
5. A product according to claim 1 or 2, characterised in that a part of its pores consists of micropores.
6. A method according to claim 1 for the production of a porous cellulosic product, characterised at least by the following production steps:
 - a) water-glass and viscose are blended into a multi-component solution
 - b) the multi-component solution is precipitated into the desired form as a solid precursor consisting of viscose which contains silicic acid
 - c) the solid precursor of viscose which contains silicic acid is extracted with an alkali in order to produce a porous cellulosic product.
7. A method according to claim 6, characterised in that at step a) water-glass and viscose are blended into a multi-

component solution with a silicic acid content of 1 to 50 percent by weight and preferably 10 to 45 percent by weight.

8. A method according to claim 6 or 7, characterised in that at step b) the multi-component solution is precipitated into the desired form by forcing it through one or more orifices such as but not restricted to spinnerettes into a regeneration bath in which it precipitates into the stated precursor product.

9. A method according to any of claims 6 to 8 individually or jointly, characterised in that the said solid precursor consisting of viscose which contains silicic acid is extracted in step c) with an alkali containing sodium hydroxide (NaOH) at a concentration of 1 to 15 percent and preferably of 5 to 10 percent.

10. A method according to any of claims 6 to 9 individually or jointly, characterised in that step d) is included in which the porous cellulosic product thus obtained is neutralised by immersion in an acid solution and preferably a dilute solution of sulphuric acid.

11. A method according to any of claims 6 to 10 individually or jointly, characterised in that the precursor obtained through step b) is a fibre, or a textile structure or a non-woven manufactured from it, or an intermediate structure for either of the last-mentioned.

12. A method according to claim 11, characterised in that the alkaline extraction of step c) is carried out on a nonwoven intermediate in which the bonding of the nonwoven fibres to each other takes place jointly with the alkaline extraction of step c).

13. The use as an hygienic wadding of a porous cellulosic product according to claims 1 to 5 or manufactured according to claims 6 to 12.

14. A product according to claim 1, characterised in that in dimensions and strength combined with each other it is capable of being processed on existing conventional textile of nonwoven machinery without substantial damage to its own physical structure.

INTERNATIONAL SEARCH REPORT

International Application No PCT/FI 92/00094

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁵ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: D 01 F 2/06, 11/02, C 08 J 9/26																	
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 25%; border-bottom: 1px solid black;">Classification System</td> <td style="border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="height: 40px; vertical-align: bottom;">IPC5</td> <td style="vertical-align: bottom;">D 01 F; C 08 J</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div> <p style="margin-top: 10px;">SE,DK,FI,NO classes as above</p>			Classification System	Classification Symbols	IPC5	D 01 F; C 08 J											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category *</th> <th style="width: 60%; border-bottom: 1px solid black;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 30%; border-bottom: 1px solid black;">Relevant to Claim No.¹³</th> </tr> <tr> <td style="vertical-align: top;">A</td> <td>GB, A, 1390061 (MAGYAR VISCOSAGYAR) 9 April 1975, see the whole document --</td> <td style="vertical-align: top;">1-14</td> </tr> <tr> <td style="vertical-align: top;">A</td> <td>GB, A, 2024827 (KURARAY CO. LTD) 16 January 1980, see the whole document --</td> <td style="vertical-align: top;">1-14</td> </tr> <tr> <td style="vertical-align: top;">A</td> <td>GB, A, 2224756 (KABUSHIKI KAISHA J.F. CORPORATION) 16 May 1990, see the whole document --</td> <td style="vertical-align: top;">1-14</td> </tr> <tr> <td style="vertical-align: top;">A</td> <td>US, A, 3565749 (IRVIN WIZON, SWARTHMORE) 23 February 1971, see the whole document -- -----</td> <td style="vertical-align: top;">1-14</td> </tr> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	GB, A, 1390061 (MAGYAR VISCOSAGYAR) 9 April 1975, see the whole document --	1-14	A	GB, A, 2024827 (KURARAY CO. LTD) 16 January 1980, see the whole document --	1-14	A	GB, A, 2224756 (KABUSHIKI KAISHA J.F. CORPORATION) 16 May 1990, see the whole document --	1-14	A	US, A, 3565749 (IRVIN WIZON, SWARTHMORE) 23 February 1971, see the whole document -- -----	1-14
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<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="height: 30px; vertical-align: bottom;">9th July 1992</td> <td style="vertical-align: bottom;">1992 -07- 13</td> </tr> <tr> <td style="border-bottom: 1px solid black;">International Searching Authority</td> <td style="border-bottom: 1px solid black;">Signature of Authorized Officer</td> </tr> <tr> <td style="height: 40px; vertical-align: bottom; text-align: center;">SWEDISH PATENT OFFICE</td> <td style="vertical-align: bottom; text-align: center;"> Jack Hedlund </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	9th July 1992	1992 -07- 13	International Searching Authority	Signature of Authorized Officer	SWEDISH PATENT OFFICE	 Jack Hedlund							
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/FI 92/00094**

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 1390061	75-04-09	NONE	
GB-A- 2024827	80-01-16	DE-A-C- 2920762	79-12-20
		JP-C- 1428690	88-03-09
		JP-A- 54153779	79-12-04
		JP-B- 62038004	87-08-15
		US-A- 4279752	81-07-21
GB-A- 2224756	90-05-16	AU-D- 1999288	89-10-16
		EP-A- 0364582	90-04-25
		JP-A- 1246469	89-10-02
		JP-B- 3036954	91-06-04
		WO-A- 89/09304	89-10-05
US-A- 3565749	71-02-23	NONE	